



# Sulfur poisoning and regeneration of bimetallic Pd-Pt methane oxidation catalysts



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## ABSTRACT

The influence of SO<sub>2</sub> on the total oxidation of methane over Pd-Pt/Al<sub>2</sub>O<sub>3</sub> and Pd-Pt/La<sub>2</sub>O<sub>3</sub>-Y<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub>-ZrO<sub>2</sub> catalysts under typical lean burn gas engine conditions was investigated and compared to engine-aged samples. Differences in deactivation rate and in stability of poisoning species were identified at 400 °C and 450 °C. A positive effect of higher pressure, related to pre-turbo positioning of the catalyst, on the activity was observed. Realistic pre-turbo conditions including high temperature (600 °C) and high pressure (4 bar) were found to favor methane conversion but even under these conditions some deactivation took place due to formation of strongly bound sulfur species and probably due to sintering of the noble metal particles. Engine aged samples were obtained after 60 h on an SO<sub>2</sub> containing exhaust-gas of a lean-burn gas engine at 450 °C. Laboratory tests with these samples revealed high accumulation of sulfur species with a higher concentration at the catalyst inlet than the outlet. Different regeneration strategies for SO<sub>2</sub> poisoned catalysts were successfully applied. Rich conditions led to very pronounced regeneration at 550 °C of a poisoned Pd-Pt/La<sub>2</sub>O<sub>3</sub>-Y<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub>-ZrO<sub>2</sub> catalyst. Short rich pulses were even able to regenerate the catalyst during operation at the gas engine. Periodic switches to  $\lambda < 1$  finally stabilized a methane conversion above 65% for several hours demonstrating the good transferability of lab test data to the engine tests.

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## 1. Introduction

Lean burn gas engines and dual fuel engines enjoy growing popularity due to low costs and still high availability of natural gas. Furthermore, they provide high fuel efficiency and emit less CO<sub>2</sub> than Diesel or gasoline engines due to a higher H:C ratio in the gaseous fuel mostly consisting of methane. Moreover, gas engines used in stationary applications as well as in mobile applications have demonstrated lower NO<sub>x</sub> and PM emissions as compared to conventional Diesel engines. Nevertheless, gas engines emit low amounts of unburned methane, whose greenhouse activity is over 20 times higher than that of CO<sub>2</sub>, which calls for the use of an exhaust-gas after-treatment catalyst [1]. So far, significant conversion under typical exhaust-gas conditions is only achieved by noble metal based catalysts [2–4]. Palladium is reported to show the highest low temperature activity for total oxidation of methane [3,5,6]. The activity of supported Pd-based catalysts depends on

many different parameters like the support material, Pd phase, gas composition or catalyst history. Thus, PdO or Pd-PdO pairs have been reported to be the most active phases [2,7–11] and the addition of small amounts of Pt was found to have beneficial effects on the activity [12] as well as on the stability [13,14].

However, methane oxidation on such catalysts is very sensitive to the gas atmosphere composition. A strong inhibition of H<sub>2</sub>O combined with long-term deactivation has been observed for Pd-based catalysts in a gas mixture containing only CH<sub>4</sub>, O<sub>2</sub> and H<sub>2</sub>O [15–17]. This was mainly attributed to the formation of surface hydroxyls on the noble metals or support surfaces [15,18]. The H<sub>2</sub>O-induced inhibition effect is present also at high pressures, characteristic for a pre-turbine positioning of the CH<sub>4</sub>-oxidation catalyst [19]. Furthermore, the main challenge of Pd-Pt catalysts remains the poisoning by sulfur containing compounds. SO<sub>2</sub> or H<sub>2</sub>S, which can be present in the exhaust-gas from the gaseous fuel itself, formed from added odorizers or from lubricants used in the engine [6,20], were identified as strong poisons for Pd-based oxidation catalysts [20,21]. Under lean conditions and at elevated temperature, SO<sub>2</sub> leads to the formation of sulfates and sulfites on both the noble metal active phase and the support [21–23]. Additionally, the formation of surface sulfates and/or sulfites as well as the amount of stored sulfur

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depends on the noble metal particle size [24]. The rate of deactivation depends on the support material. Sulfating supports like alumina can act as scavenger protecting the active sites by formation of sulfates on the support. This effect slows down the poisoning process but also prolongs the process of regeneration [6,23]. On non-sulfating supports such as  $\text{SiO}_2$ , the active phase is not protected leading to fast deactivation. However, regeneration is faster since only small amounts of sulfur species are present on the poisoned catalyst [23]. Different procedures for regeneration are also discussed in literature, which include high temperature treatment and rich conditions [25–29]. Jones et al. [25] for example showed that poisoned  $\text{Pd}/\text{Al}_2\text{O}_3$  can be partially regenerated by exposure to  $\text{H}_2$  at  $400^\circ\text{C}$ . The reduction of surface sulfates and the subsequent release of  $\text{SO}_2$  were linked to the high efficiency of regeneration.

Although catalyst deactivation is multifaceted under real engine conditions, only few studies have been so far reported particularly on real engine deactivation [20,30]. Hence, in this work, the effects of the supporting material and operating conditions on the  $\text{SO}_2$ -deactivation extent and regeneration ability were investigated by both laboratory and engine tests. The methane oxidation activity of  $\text{Pd-Pt}/\text{Al}_2\text{O}_3$  and  $\text{Pd-Pt}/\text{La}_2\text{O}_3\text{-Y}_2\text{O}_3\text{-CeO}_2\text{-ZrO}_2$  catalysts was evaluated under different temperatures and pressures including the regeneration by reductive treatment. Finally, the outcome of the laboratory tests regarding catalyst deactivation and regeneration was transferred to engine dynamometer experiments.

## 2. Experimental

### 2.1. Catalytic materials

Three different Pd-Pt based catalysts deposited on  $\text{Al}_2\text{O}_3$  and on Y-, La-doped  $\text{CeO}_2\text{-ZrO}_2$  were used in the form of powders or coated monoliths in this study:

- 1) A commercial catalyst supplied by Johnson Matthey plc consisting of palladium and platinum (Pd:Pt 5:1 weight ratio) on an alumina based support (referred to as  $\text{Pd-Pt}/\text{Al}_2\text{O}_3$  in this study). Ceramic monoliths with 230 cpsi and a noble metal loading of  $120\text{ g/ft}^3$  were used for the catalytic tests.
- 2) A 2.4 wt.% Pd-Pt/ $\text{ZrO}_2\text{-CeO}_2\text{-Y}_2\text{O}_3\text{-La}_2\text{O}_3$  (Pd:Pt 5:1 weight ratio) denoted powdered Pd-Pt/CZ-sample, which was prepared by incipient wetness impregnation of a commercial  $\text{Y}_2\text{O}_3\text{-La}_2\text{O}_3\text{-CeO}_2\text{-ZrO}_2$  mixed oxide (metal weight ratios 5:5:30:60 in following referred to as CZ), calcined at  $700^\circ\text{C}$  for 5 h in static air prior to the synthesis. An aqueous solution of tetraamminepalladium(II) nitrate and tetraammineplatinum(II) nitrate was used for the impregnation of the carrier. Two steps with 5 h of drying at room temperature and 1 h at  $70^\circ\text{C}$  in between were needed to obtain the total noble metal loading of 2.4 wt.%. After the final step and drying at  $70^\circ\text{C}$  for 12 h, the resulting sample was calcined in static air at  $500^\circ\text{C}$  for 5 h.
- 3) An additional catalyst consisting of 2.4 wt.% Pd-Pt/ $\text{La}_2\text{O}_3\text{-Y}_2\text{O}_3\text{-CeO}_2\text{-ZrO}_2$ , which was prepared by industrial partners according to the procedure as the described for the catalyst in 2. The catalyst was washcoated on metallic substrates with 400 cpsi to obtain a noble metal loading of  $100\text{ g/ft}^3$ . Samples with 25 mm length and 25 mm diameter were used for laboratory test bench tests and samples with 130 mm length and 120 mm diameter for engine tests, denoted as monolithic Pd-Pt/CZ-sample

### 2.2. Catalyst characterization

The surface area was determined by  $\text{N}_2$  physisorption at  $-196^\circ\text{C}$  according to the Brunauer-Emmet-Teller method [31] on a BELSOPRP-mini instrument (MicrotracBEL, Osaka, Japan). Prior to the analysis, the sample was degassed at  $300^\circ\text{C}$  for 2 h.

X-ray diffraction (XRD) patterns were recorded using a Bruker Advance D8 diffractometer with  $\text{Cu K}\alpha$  radiation (wavelength =  $1.54\text{ \AA}$ ). The patterns were recorded between  $20^\circ$  to  $90^\circ$  with a step size of  $0.016^\circ$  and an acquisition time of 0.51 s per point.

Temperature Programmed Desorption of sulfur (S-TPD) was performed by heating the samples with 10 K/min from room temperature to  $925^\circ\text{C}$  in 5 L/min  $\text{N}_2$  (dosed via Bronkhorst mass flow controllers) and keeping them at this temperature for 30 min. Desorption products were monitored using a Fourier transform infrared spectrometer (FTIR, Multigas MG2030, MKS). Although  $\text{SO}_2$  and  $\text{SO}_3$  were monitored as sulfur containing species, only  $\text{SO}_2$  desorption profiles are reported since no  $\text{SO}_3$  could be detected during TPD.

The particle size and chemical composition of the catalyst was studied by High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) in combination with energy-dispersive X-ray spectroscopy (EDXS) using an FEI OSIRIS ChemiSTEM microscope at 200 kV acceleration voltage. The microscope is equipped with a high brightness electron source and four BRUKER Silicon drift detectors (SDD) for high efficiency collection efficiency and high counting rates, especially eligible for characterizing chemical composition of nanoparticles. TEM samples are prepared by deposition of particles on an amorphous carbon (Lacey-) film copper grid. EDXS spectra were acquired by either scanning a rectangular sample area (EDXS mapping) containing numerous particles and summing up the X-ray counts (average composition), or by measuring single NP (spot measurement; individual composition of the characterized NP). Quantification of the EDX spectra was performed with the BRUKER software package ESPRIT, using the Pd-L and Pt-L lines. Element concentrations were derived on basis of the Cliff-Lorimer approximation, implemented in the ESPRIT software.

### 2.3. Tests on catalyst test bench

#### 2.3.1. General procedure

For honeycombs, the catalyst sample (diameter 2 cm, length between 2 and 5 cm) was placed inside of a plug flow reactor (made from quartz glass or coated stainless steel for tests at higher pressure) and fixed with quartz glass wool. For powdered catalysts, a bed of 1.5 cm length fixed by quartz glass wool was obtained by diluting 300 mg of catalyst ( $125\text{--}250\text{ }\mu\text{m}$  sieve fraction) with 700 mg quartz sand balls ( $125\text{--}250\text{ }\mu\text{m}$ ). For all tests, the temperature was monitored by two thermocouples placed about 5 mm upstream and downstream of the catalyst. Reactor heating and cooling was done by Eurotherm controllers based on the thermocouple located upstream of the catalyst bed. The gas mixture was fed by Bronkhorst MFCs and the reaction products were monitored by a FT-IR spectrometer (Multigas 2030, MKS). Light-off experiments consisting of heating-cooling cycles were performed with 3 K/min between  $225^\circ\text{C}$  and  $525^\circ\text{C}$  under “dry” (3200 ppm  $\text{CH}_4$ , 10%  $\text{O}_2$  in  $\text{N}_2$ ) or “wet” (3200  $\text{CH}_4$ , 10%  $\text{O}_2$ , 12%  $\text{H}_2\text{O}$  in  $\text{N}_2$ ) conditions.

#### 2.3.2. Deactivation in $\text{SO}_2$ containing atmospheres

Deactivation experiments at different temperatures ( $400^\circ\text{C}$  and  $450^\circ\text{C}$ ) and varying  $\text{SO}_2$  concentration (2.5 ppm and 5 ppm) were performed using the  $\text{Pd-Pt}/\text{Al}_2\text{O}_3$  honeycomb catalysts.

An experiment consisted of: (i) a light-off experiment in the fresh state between  $225^\circ\text{C}$  and  $525^\circ\text{C}$  (3 K/min) with 3200 ppm  $\text{CH}_4$ , 10%  $\text{O}_2$  and 12%  $\text{H}_2\text{O}$  in  $\text{N}_2$  (“wet”); (ii) 25 h at  $400^\circ\text{C}$  or  $450^\circ\text{C}$  with 2.5 or 5 ppm  $\text{SO}_2$  added and (iii) a second light-off experiment subsequently up to  $550^\circ\text{C}$  in “wet” reaction mixture. To check the catalyst stability in absence of  $\text{SO}_2$ , an additional experiment was performed for 25 h at  $400^\circ\text{C}$  with 3200 ppm  $\text{CH}_4$ , 10%  $\text{O}_2$  and 12%  $\text{H}_2\text{O}$  in  $\text{N}_2$ . For every test a fresh sample was used and degreened

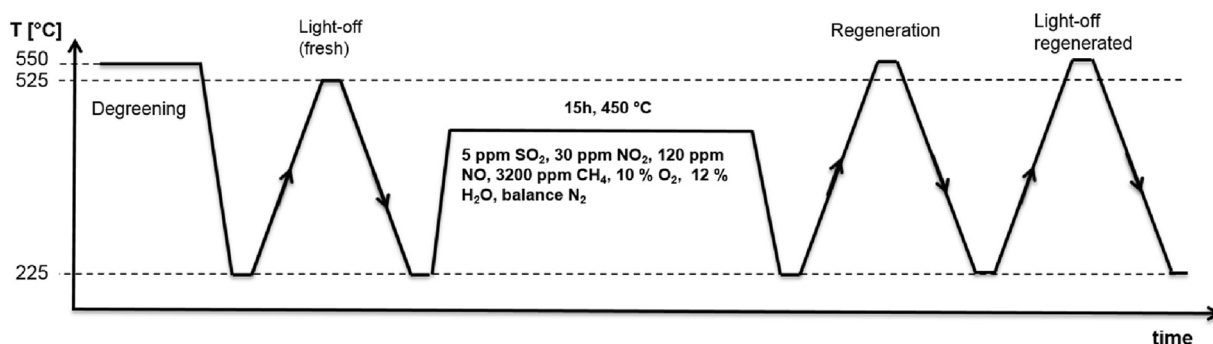


Fig. 1. Reaction protocol for regeneration experiments.

Table 1

Engine and exhaust parameters for lean catalyst tests on the engine bench.

revolutions per minute	Lambda [–]	Temp. catalyst inlet [°C]	Temp. catalyst outlet [°C]	GHSV [h <sup>–1</sup> ]	CH <sub>4</sub> [ppm]	CO [ppm]	CO <sub>2</sub> [%]	O <sub>2</sub> [%]	S [ppm] <sup>a</sup>
1700	1.68	451	319	80,000	2680	660	7.5	7.7	~0.3

<sup>a</sup> calculated based on S-species in fuel (odorizer THT) and  $\lambda$ -value.

at 550 °C in 3200 ppm CH<sub>4</sub>, 10% O<sub>2</sub> in N<sub>2</sub> for 1 h prior to each run. The GHSV for these experiments was always kept at 30,000 h<sup>–1</sup>.

Tests at higher pressure were conducted to investigate conditions representing pre-turbo positioning of the catalyst [32] with monolithic Pd-Pt/Al<sub>2</sub>O<sub>3</sub> catalysts. The experiments consisted of isothermal long-term tests for 20 h at different temperatures (450 °C and 600 °C) and two different pressures (1 bar and 4 bar) in an SO<sub>2</sub> containing atmosphere (5 ppm SO<sub>2</sub>, 30 ppm NO<sub>2</sub>, 120 ppm NO, 1000 ppm CH<sub>4</sub>, 10% O<sub>2</sub>, 12% H<sub>2</sub>O in N<sub>2</sub>) with a GHSV of 60,000 h<sup>–1</sup>. For every test, a fresh sample was used. The total SO<sub>2</sub> amount entering the catalyst during 20 h on stream sums up to 3.9 mmol, which corresponds to 250 mmol SO<sub>2</sub> per liter of catalyst. Russell et al. [33] reported a completely sulfated Pt/Al<sub>2</sub>O<sub>3</sub> catalyst after 95 mmol SO<sub>2</sub> per liter of catalyst at 375 °C. Therefore, a uniform distribution of sulfur species is expected in our experiments after 20 h on stream. After the long-term tests, the monolithic samples were cut in 2 pieces with 2 cm and 3 cm length. The shorter piece was characterized performing a S-TPD and the larger piece was used for activity tests by means of light-off experiments. The light-off experiments consisted of two consecutive heating and cooling cycles between 225 °C and 525 °C in 3200 ppm CH<sub>4</sub>, 10% O<sub>2</sub> in N<sub>2</sub> at 1 bar. In contrast to the long-term tests, a GHSV of 30,000 h<sup>–1</sup> was used.

### 2.3.3. Regeneration

Regeneration experiments consisted of a light-off in the fresh state (after degreening) in “wet” reaction conditions; deactivation at 450 °C with 5 ppm SO<sub>2</sub>, 30 ppm NO, 120 ppm NO<sub>2</sub>, 3200 ppm CH<sub>4</sub>, 10% O<sub>2</sub>, 12% H<sub>2</sub>O in N<sub>2</sub>; regeneration during light-off in different SO<sub>2</sub>-free gas atmospheres and a consecutive light-off in SO<sub>2</sub>-free “wet” reaction conditions. Details on the procedure are given in Fig. 1. The tests were performed at a GHSV of 30,000 h<sup>–1</sup> for monolithic samples or 1 L/min, which corresponds to a GHSV of 80,000 h<sup>–1</sup> relative to the catalyst bed volume, for powdered samples. Three different regeneration atmospheres were investigated, i.e.:

- reaction mixture: 3200 ppm CH<sub>4</sub>, 10% O<sub>2</sub>, 12% H<sub>2</sub>O in N<sub>2</sub> (referred to as “RM”),
- lean conditions: 10% O<sub>2</sub>, 12% H<sub>2</sub>O in N<sub>2</sub> (referred to as “lean”), and
- rich conditions: 3200 ppm CH<sub>4</sub>, 12% H<sub>2</sub>O in N<sub>2</sub> (referred to as “rich”).

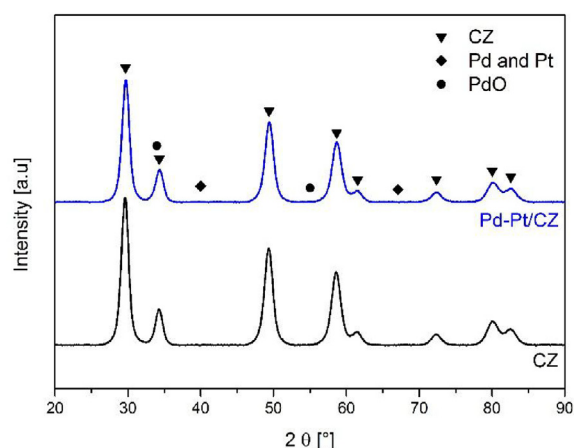


Fig. 2. XRD patterns of 2.4 wt.% powdered Pd-Pt/CZ (Pd:Pt 5:1) and pure CZ support material.

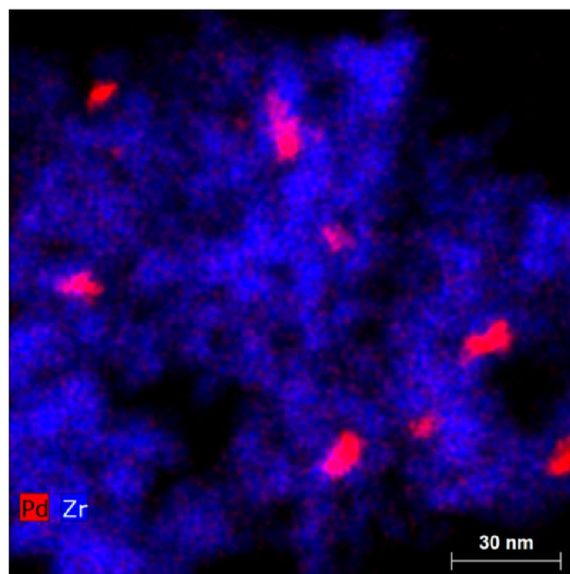
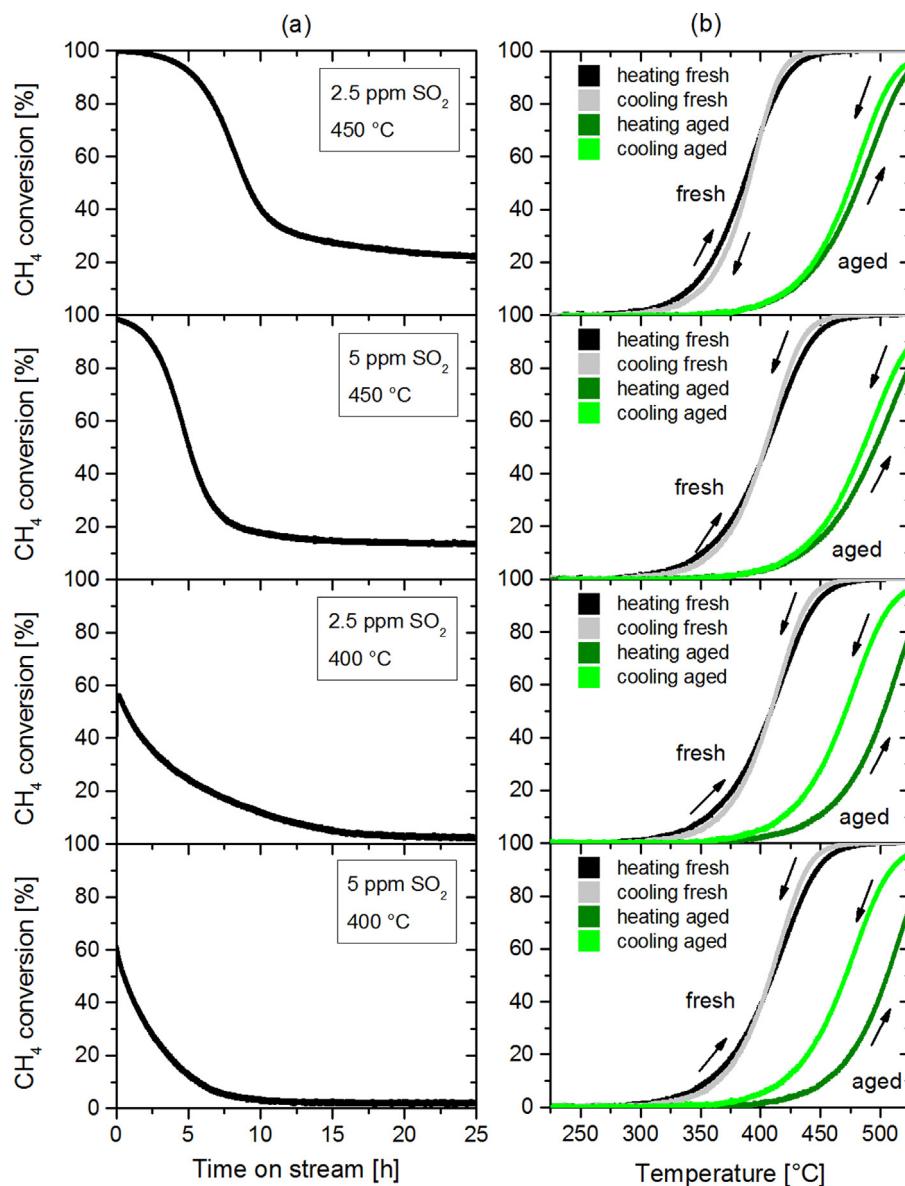


Fig. 3. HAADF STEM image with colour code for Pd and Zr obtained from EDX scans of the 2.4 wt.% powdered Pd-Pt/CZ sample.



**Fig. 4.** (a) CH<sub>4</sub> conversion as function of time on stream over Pd-Pt/Al<sub>2</sub>O<sub>3</sub> at two different temperatures (400 °C and 450 °C) and two SO<sub>2</sub> concentrations (2.5 ppm and 5 ppm). (b) CH<sub>4</sub> conversion profiles before (fresh) and after 25 h time on stream (aged). Gas composition for light-offs: 3200 ppm CH<sub>4</sub>, 10% O<sub>2</sub>, 12% H<sub>2</sub>O in N<sub>2</sub>. For the long-term tests 2.5 ppm or 5 ppm SO<sub>2</sub> were added. GHSV = 30,000 h<sup>-1</sup>.

Additionally, a regeneration experiment under isothermal conditions was carried out at 450 °C with the powdered Pd-Pt/CZ sample. After complete deactivation in 5 ppm SO<sub>2</sub>, 30 ppm NO, 120 ppm NO<sub>2</sub>, 3200 ppm CH<sub>4</sub>, 10% O<sub>2</sub>, 12% H<sub>2</sub>O in N<sub>2</sub>, different parameters were varied i.e. turn off SO<sub>2</sub> or O<sub>2</sub> at this temperature. Next, the catalyst was heated to 500 °C and 550 °C for one hour in SO<sub>2</sub> free reaction atmosphere. Furthermore, rich conditions were investigated at 500 °C and 550 °C for one hour, which have been realized by stopping O<sub>2</sub> dosage. Between these changes, the catalyst was kept at 450 °C in 5 ppm SO<sub>2</sub>, 30 ppm NO, 120 ppm NO<sub>2</sub>, 3200 ppm CH<sub>4</sub>, 10% O<sub>2</sub>, 12% H<sub>2</sub>O in N<sub>2</sub> for several hours to ensure total deactivation before performing the regeneration steps. The overall flow of 1 L/min was always kept constant by balancing with N<sub>2</sub>.

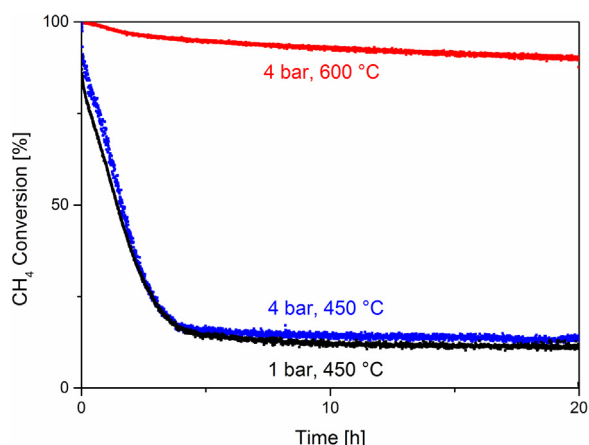
#### 2.4. Tests on engine test bench

The monolithic Pd-Pt/CZ catalyst was placed downstream of a 1.4 l 4 cylinder TSI engine running on compressed natural gas

(CNG). Temperature was measured upstream and downstream of the catalyst as well as gaseous reaction products using a National Instruments test bed control and measurement system, a Siemens Ultramat 6 methane analyzer and a SUN DGA 1500 5 component exhaust-gas analyzer.

A deactivation experiment consisted of a long-term run for 60 h at a constant engine operating point. The relevant engine and exhaust-gas parameters are summarized in Table 1. The engine test was performed within 10 days with about 6 h runs per day. After that, samples with 25 mm in diameter and 42 mm length were drilled out from the catalyst at three different radial and axial positions (Fig. 12). Three equivalent catalyst samples for every axial position were obtained, since no differences in catalyst deactivation are expected in radial direction. The samples are denoted as Pos 1 (catalyst inlet), Pos 2 (catalyst middle) and Pos 3 (catalyst outlet). The samples were investigated by means of light-off tests in “dry” reaction mixture (3200 ppm CH<sub>4</sub>, 10% O<sub>2</sub> in N<sub>2</sub>) with a GHSV of 30,000 h<sup>-1</sup>. A second set of samples was characterized by S-TPD.





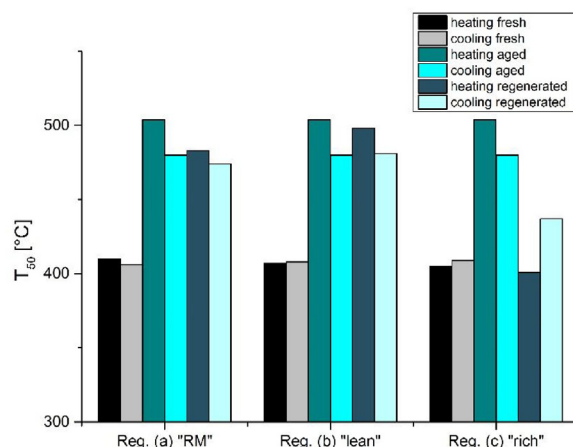
**Fig. 5.** Methane conversion of Pd-Pt/Al<sub>2</sub>O<sub>3</sub> during 20 h time on stream at 1 bar and 4 bar at 450 °C and 600 °C. Gas composition: 5 ppm SO<sub>2</sub>, 30 ppm NO<sub>2</sub>, 120 ppm NO, 1000 ppm CH<sub>4</sub>, 10% O<sub>2</sub>, 12% H<sub>2</sub>O in N<sub>2</sub>. GHSV = 60,000 h<sup>-1</sup>.

In a second test series, a fresh monolithic Pd-Pt/CZ catalyst was mounted and a long-term run including regeneration was conducted. Initially a steady state test was performed at the same operating point as shown in Table 1 to create catalyst deterioration. After 12 h, the engine controller was set at an increased fuel amount to cross the  $\lambda = 1$  limit for 30 min. To keep exhaust-gas temperature at the same level, the load was reduced during rich run, lowering the space velocity to about 50,000 h<sup>-1</sup>. After 30 min rich operation, the engine was run again at  $\lambda = 1.68$  for several hours. Short rich pulses for 1 and 5 min were performed while always switching back to lean operation for several minutes in between.

### 3. Results and discussion

#### 3.1. Characterization

X-ray diffraction patterns of the Pd-Pt/CZ powdered catalyst and of the pure CZ support as reference are displayed in Fig. 2. The symmetric reflections of the support material are shifted to lower angles compared to pure ZrO<sub>2</sub> indicating the existence of a solid solution with CeO<sub>2</sub> [34]. No reflections for PdO or Pd/Pt were found in the impregnated sample, most probably because the noble metal particles are highly dispersed on the support. This observation is in



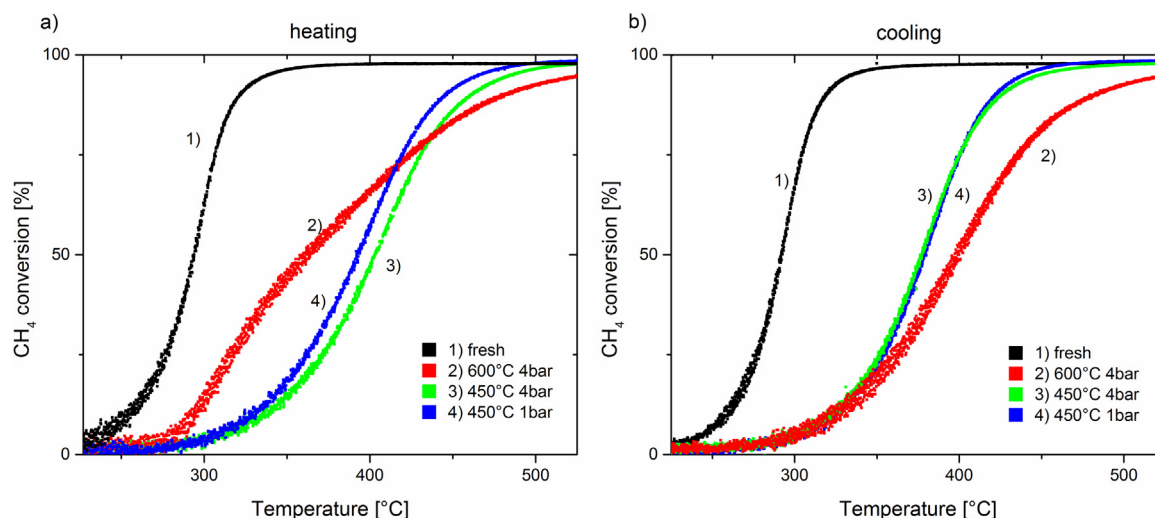
**Fig. 7.** T<sub>50</sub> in fresh, aged and regenerated state (bars from left to right) during heating and cooling for three different regeneration experiments on Pd-Pt/Al<sub>2</sub>O<sub>3</sub> catalyst. Gas composition for deactivation at 450 °C for 15 h: 5 ppm SO<sub>2</sub>, 30 ppm NO<sub>2</sub>, 120 ppm NO, 3200 ppm CH<sub>4</sub>, 10% O<sub>2</sub>, 12% H<sub>2</sub>O in N<sub>2</sub>. Gas composition for regeneration (consisting of heating and consecutive cooling between 225 °C and 550 °C): a) "RM": 3200 ppm CH<sub>4</sub>, 10% O<sub>2</sub>, 12% H<sub>2</sub>O in N<sub>2</sub>. "lean": 10% O<sub>2</sub>, 12% H<sub>2</sub>O in N<sub>2</sub>. b) "rich": 3200 ppm CH<sub>4</sub>, 12% H<sub>2</sub>O in N<sub>2</sub>. c) GHSV = 30,000 h<sup>-1</sup>.

accordance with electron microscopy showing noble metal particles with sizes between 1 and 2 nm, partially agglomerated (Fig. 3). EDX scans of the NM particles revealed the presence of pure Pd particles as well as bimetallic Pd-Pt-particles with compositions of 3–10% Pt. The BET surface area of the powdered Pd-Pt/CZ was found to be 75 m<sup>2</sup>/g. The commercial Pd-Pt/Al<sub>2</sub>O<sub>3</sub> sample could not be characterized for IP reasons.

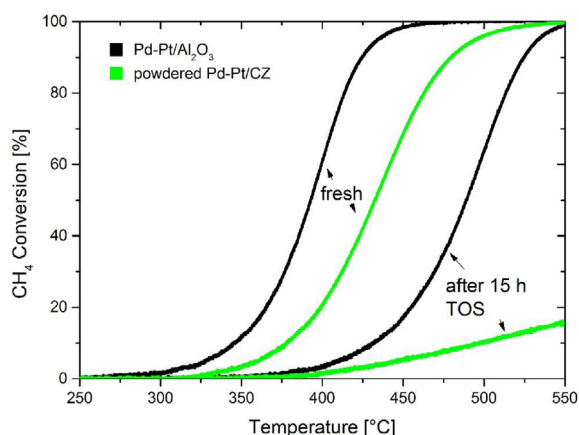
#### 3.2. Laboratory catalyst tests

##### 3.2.1. Catalytic performance and influence of temperature on deactivation of monolithic Pd-Pt/Al<sub>2</sub>O<sub>3</sub> in a SO<sub>2</sub> containing model gas

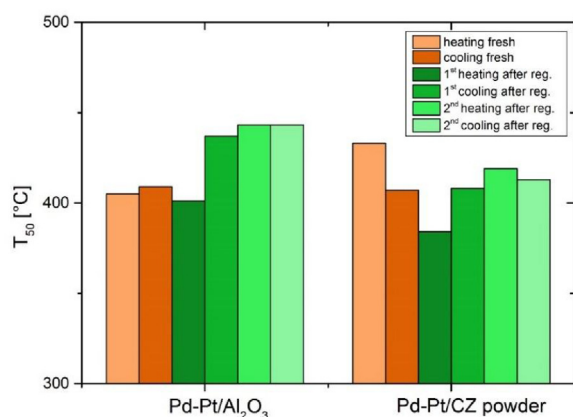
In the fresh state, the Pd-Pt/Al<sub>2</sub>O<sub>3</sub> catalyst shows a typical methane conversion profile for Pd-based catalysts in the presence of H<sub>2</sub>O (Fig. 4a). The light-off temperature (temperature of 50% methane conversion, T<sub>50</sub>) was around 405 °C and full conversion was reached above 450 °C. As previously reported, the presence of SO<sub>2</sub> in the gas stream strongly affects the activity in a negative way



**Fig. 6.** CH<sub>4</sub> conversion profiles of fresh Pd-Pt/Al<sub>2</sub>O<sub>3</sub> and after time on stream in SO<sub>2</sub> containing atmosphere at different temperatures and pressure. Gas composition: 3200 ppm CH<sub>4</sub>, 10% O<sub>2</sub> in N<sub>2</sub>. GHSV = 30,000 h<sup>-1</sup>. (a) heating (b) consecutive cooling.



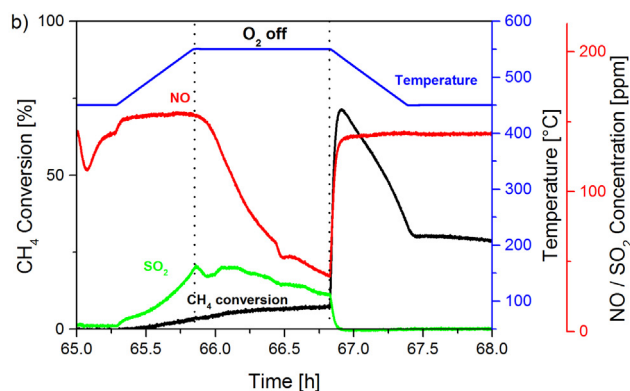
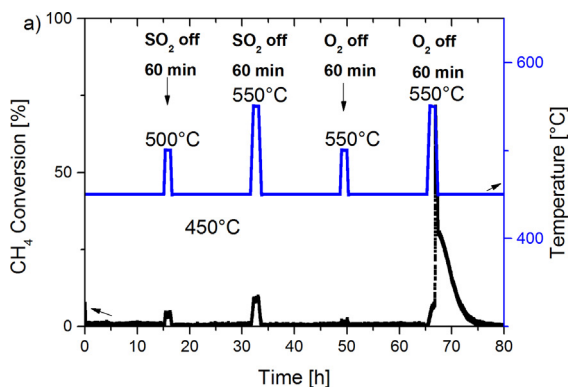
**Fig. 8.** Methane conversion over Pd-Pt/Al<sub>2</sub>O<sub>3</sub> and powdered Pd-Pt/CZ in 3200 ppm CH<sub>4</sub>, 10% O<sub>2</sub>, 12% H<sub>2</sub>O, balance N<sub>2</sub> with 3 K/min. Fresh samples and samples after 15 h time on stream (TOS) in 5 ppm SO<sub>2</sub>, 30 ppm NO<sub>2</sub>, 120 ppm NO, 3200 ppm CH<sub>4</sub>, 10% O<sub>2</sub>, 12% H<sub>2</sub>O in N<sub>2</sub> are shown. For monolithic Pd-Pt/Al<sub>2</sub>O<sub>3</sub> GHSV = 30,000 h<sup>-1</sup>. For powdered Pd-Pt/CZ GHSV = 80,000 h<sup>-1</sup>.



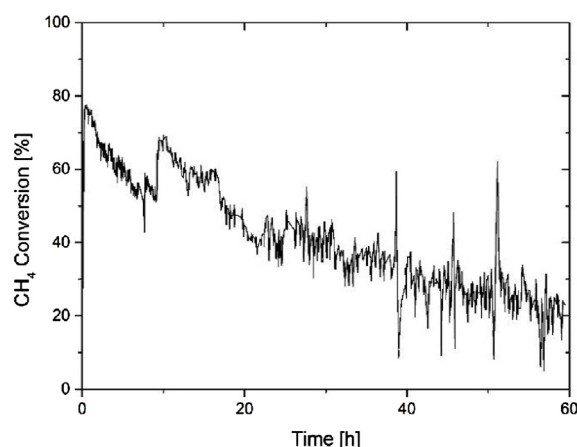
**Fig. 9.** T<sub>50</sub> during light-off (heating/cooling) with 3200 ppm CH<sub>4</sub>, 10% O<sub>2</sub>, 12% H<sub>2</sub>O in N<sub>2</sub> in the fresh state and regenerated after 15 h time on stream in 5 ppm SO<sub>2</sub>, 30 ppm NO<sub>2</sub>, 120 ppm NO, 3200 ppm CH<sub>4</sub>, 10% O<sub>2</sub>, 12% H<sub>2</sub>O in N<sub>2</sub>. Regeneration consisted of heating/cooling between 225 °C and 550 °C in 3200 ppm CH<sub>4</sub>, 12% H<sub>2</sub>O in N<sub>2</sub>. GHSV = 30,000 h<sup>-1</sup> for Pd-Pt/Al<sub>2</sub>O<sub>3</sub> and 80,000 h<sup>-1</sup> for Pd-Pt/CZ powder.

[6,16,17,27,28,35,36]. Fig. 4 shows the CH<sub>4</sub> conversion trend during deactivation and light-off behavior in fresh and deactivated state for Pd-Pt/Al<sub>2</sub>O<sub>3</sub>.

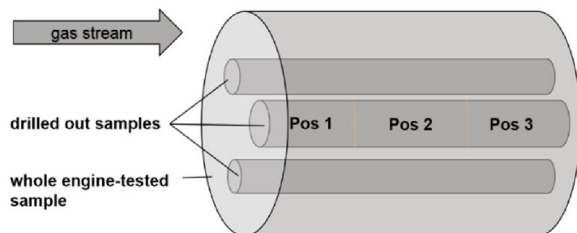
At 450 °C in the presence of 2.5 ppm SO<sub>2</sub>, a rapid drop in CH<sub>4</sub> oxidation activity is observed within the first 5 h but the poisoning



**Fig. 10.** (a) CH<sub>4</sub> conversion of powdered Pd-Pt/CZ as function of time at 450 °C. Standard gas composition: 5 ppm SO<sub>2</sub>, 30 ppm NO<sub>2</sub>, 120 ppm NO, 3200 ppm CH<sub>4</sub>, 10% O<sub>2</sub>, 12% H<sub>2</sub>O in N<sub>2</sub>. Flow: 1 L/min. Changes in gas composition and temperature according to figure. Overall flow always kept constant by balancing with N<sub>2</sub>. Catalyst experienced standard gas composition for approximately 25 h prior to this figure. (b) Detailed demonstration of gas concentrations and temperature between 65 and 68 h time on stream.



**Fig. 11.** CH<sub>4</sub> conversion over monolithic Pd-Pt/CZ catalyst operating on a gas engine running at λ = 1.68. Engine exhaust-gas composition: ~0.3 ppm SO<sub>2</sub>, 170 ppm NMHC, 660 ppm CO, 2680 ppm CH<sub>4</sub>, 7.7% O<sub>2</sub>, H<sub>2</sub>O (concentration not known). Temperature at catalyst inlet: 450 °C. GHSV = 80,000 h<sup>-1</sup>.



**Fig. 12.** Schematic drawing of cylindrical cores with 25 mm diameter and 42 mm length obtained from bigger monolithic Pd-Pt/CZ sample operated for 60 h on lean gas engine exhaust-gas and the labelling of corresponding samples.

is still occurring after 25 h on stream. For the case of 5 ppm SO<sub>2</sub>, a much steeper decrease is noticed during the first 3 h and the deactivation process slows down after 10 h. Under these conditions, a steady state seems to be reached after 25 h. The overall decrease is almost the same after 25 h on stream poisoning, as the conversion dropped to only 21% for a 2.5 ppm SO<sub>2</sub> concentration and to 17% for 5 ppm SO<sub>2</sub>.

At 400 °C, as soon as the catalyst was exposed to the SO<sub>2</sub> containing gas stream at t = 0 h, the conversion dropped immediately and reached almost 0% after 25 h time on stream, being faster with higher SO<sub>2</sub> concentration in the gas stream. The rate of deactivation, which was found to depend on the total amount of SO<sub>2</sub> in the gas mixture, is in line with previous studies on Al<sub>2</sub>O<sub>3</sub> supported cat-

alysts [17]. In fact, conversion profiles in presence of 2.5 and 5 ppm SO<sub>2</sub> plotted over the total amount of SO<sub>2</sub> entering the catalyst, superimpose perfectly (Fig. S1). As widely discussed, the reason for the pronounced deactivation is the formation of different sulfur species on the surface of the noble metals [22] as well as on the Al<sub>2</sub>O<sub>3</sub> support [23,24]. Under lean conditions and in the presence of Pd and especially of Pt [37], the oxidation of SO<sub>2</sub> to SO<sub>3</sub> occurs, which is able to form inactive surface/bulk PdSO<sub>4</sub> [23,38].

The difference between deactivation at 400 °C and 450 °C was further revealed by the following light-off tests (Fig. 4b). During heating, the samples deactivated at higher temperature showed a lower light-off temperature than the ones deactivated at 400 °C. Comparing the tests after poisoning with 5 ppm SO<sub>2</sub>, where a complete poisoning can be assumed, the sample deactivated at 450 °C exhibited a T<sub>50</sub> that is 10 K lower as compared to the sample treated at 400 °C (T<sub>50</sub> = 496 °C vs. T<sub>50</sub> = 506 °C). The 25 h on stream at 400 °C must have led to a more efficient poisoning of the active sites. Similar behavior was observed by Yu and Shaw [39] on Pd/Al<sub>2</sub>O<sub>3</sub> catalysts when comparing the activity of samples poisoned at 200, 300 and 400 °C. A possible explanation is a two step deactivation process, which leads to the formation of sulfates. First the adsorption of SO<sub>2</sub> occurs, which is favored at lower temperature followed by the oxidation to SO<sub>3</sub> [40] leading to sulfates which is faster at higher temperature. At higher temperatures the spillover to the support is favored, resulting in formation of bulk Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> [41]. This phenomenon could explain the higher activity of the catalyst poisoned at 450 °C. In this case, more active PdO is present since more sulfur species are transferred to the support than at 400 °C. Another explanation might be the continuous deactivation caused by the presence of water (12% water was present in the tests). As widely discussed in literature, Pd based catalysts suffer from deactivation caused by formation of surface hydroxyl groups [15,17,18,42]. This process is more pronounced at lower temperature and might add to the observed lower catalytic activity after time on stream at 400 °C. In fact, a baseline experiment at 400 °C in absence of SO<sub>2</sub> revealed the loss of CH<sub>4</sub> oxidation activity during 25 h on stream. The deactivation is much slower compared to the case if small amounts of SO<sub>2</sub> are present and the conversion stabilizes at around 30% after 20 h (Fig. S2).

However, comparing the consecutive cooling curves from 525 °C to 225 °C, the sample deactivated at 400 °C is much more active than the one deactivated at 450 °C, which is displayed by a pronounced inverse hysteresis in Fig. 4b; 400 °C. During the heating cycle, which was conducted in the absence of SO<sub>2</sub>, this sample experienced a more pronounced regeneration. This observation could be explained by the presence of less stable sulfur species formed on Pd and Pt at 400 °C, e.g. sulfites/SO<sub>2</sub> instead of stable sulfates. During the light-off experiment, these less stable S-species must have been decomposed or transferred to the support material at higher temperature leading to a larger number of free active sites during the consecutive cooling. This conclusion is supported by the detection of higher amounts of SO<sub>2</sub> during heating for samples deactivated at 400 °C compared to those deactivated at 450 °C (Fig. S3). Similar results were found by Ordonez et al. [36] who reported sulfite formation at lower temperature based on TPO experiments of poisoned Pd/Al<sub>2</sub>O<sub>3</sub> catalysts.

### 3.2.2. Influence of different pressures on the activity and stability of monolithic Pd-Pt/Al<sub>2</sub>O<sub>3</sub>

A potential positioning of the catalyst in front of the turbocharger changes the operating conditions for the catalytic converter [19,32,43]. Under pre-turbo conditions, on the one hand, the temperatures are generally higher. On the other hand, the pressure is typically in the range of 3–5 bar for lean operating gas engines. At constant mass flow, the higher pressure leads to an increased residence time for the gaseous species inside the cat-

alyst channels, but also to a slower diffusion. Hence, radial mass transport may limit the reaction rate at higher pressure [44].

Fig. 5 shows the methane conversion as function of time for different pressures and temperatures. The increase of pressure from 1 to 4 bar at 450 °C led to a higher initial conversion followed by fast deactivation. The CH<sub>4</sub> conversion curves vs. time are quite similar and a conversion of only 11% after 20 h at 1 bar and 13% at 4 bar was measured. This can be explained by a longer residence time in the 4 bar case leading to higher conversion. As reported in earlier studies [19] the negative effect of slower diffusion does not play a major role in this temperature range for small channel diameters and washcoat thicknesses. A negative effect of higher partial pressure of SO<sub>2</sub> was not detected at 450 °C and 4 bar as well, which is in agreement with findings in the previous section, where the rate of deactivation was found to be linearly depending on the amount of SO<sub>2</sub> entering the catalyst (Fig. S1).

The test conducted at 600 °C and 4 bar, which represents typical pre-turbo conditions, shows a different CH<sub>4</sub> conversion trend. The higher temperature and therefore higher catalyst activity resulted in a CH<sub>4</sub> conversion higher than 90% during 20 h on stream. However, even at 600 °C, some decrease of activity was observed leading to the hypothesis that SO<sub>2</sub> poisoning plays a role at higher temperature as well. In addition, sintering of the noble metals in an SO<sub>2</sub>-containing atmosphere [45] might have led to a slight decrease in CH<sub>4</sub> conversion at 600 °C. Monai et al. [46] reported also deactivation of a Pd/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst in SO<sub>2</sub> containing atmosphere at 600 °C and detected sulfate formation. Deactivation due to the presence of water is not expected to play a role at this high temperature, particularly in the presence of NO and NO<sub>2</sub> [17,42].

When comparing the fresh sample with the samples after 20 h on SO<sub>2</sub> poisoning stream, a pronounced shift in light-off temperature can be observed (Fig. 6). While during the first heating, the sample from the test at 600 °C and 4 bar seems to be more active in low temperature range, its CH<sub>4</sub> oxidation activity was significantly shifted to higher temperatures during cooling down. This could be due to a more pronounced spillover of sulfates to the alumina during time on stream in SO<sub>2</sub> containing atmosphere during deactivation at 600 °C leading to less poisoned Pd-sites. At increasing temperatures during CH<sub>4</sub> light-off (SO<sub>2</sub> free); the sulfur species from the support start to re-poison the active sites leading to lower activity above 400 °C and during cooling. An equilibrium between sulfur species on the active sites and on the support depending on temperature can be assumed. At temperatures above 400 °C, the species become mobile and spillover can occur. With higher temperature (600 °C), this spillover leads to free Pd sites and higher uptake of sulfur species on the Al<sub>2</sub>O<sub>3</sub>-based support. At lower temperatures (400–500 °C), the equilibrium shifts to a higher amount of poisoned noble metal sites. No SO<sub>2</sub> release was observed during the light-off experiments after poisoning at 600 °C at 4 bar, supporting the explanation that only a redistribution of sulfur species on the catalyst appeared leading to lower activity.

Comparing the samples deactivated at 450 °C, the sample that was deactivated at 4 bar was less active than the one deactivated at 1 bar, during heating. This may be explained by the adsorption of SO<sub>2</sub> or other less stable species on the palladium stabilized by the higher partial pressure of SO<sub>2</sub> leading to stronger poisoning of active sites. This hypothesis is supported by S-TPD experiments (Fig. S4) that show desorption of small amounts of SO<sub>2</sub> already at 300 °C for the 450 °C/4 bar sample compared to 500 °C for the other samples. During cooling, both samples deactivated at 450 °C exhibit the same catalytic activity and a shift to lower temperature compared to the heating cycle. Decomposition of surface sulfates that were stable below 450 °C can explain this regeneration. In fact, SO<sub>2</sub> release was detected during heating in post poisoned light-off experiments starting at around 450 °C.

During the cooling cycle, at which the transfer of sulfur species from the support to the active sites should have proceeded, the conversion below 350 °C is similar for all 3 samples. At higher temperature, the sample poisoned at 600 °C and 4 bar is less active. The fact, that the amount of SO<sub>2</sub> stored is more or less the same amount for all samples (slightly higher for 450 °C and 4 bar) indicates that the stronger deactivation is not just related to the amount of sulfates/sulfites, but to sintering of the noble metals at 600 °C [45].

### 3.2.3. Regeneration of Pd-Pt/Al<sub>2</sub>O<sub>3</sub>

Different regeneration atmospheres consisting of two lean conditions (reaction atmosphere with CH<sub>4</sub> and without CH<sub>4</sub>) and one rich composition (reaction mixture without O<sub>2</sub>) were investigated using poisoned Pd-Pt/Al<sub>2</sub>O<sub>3</sub> samples.

Fig. 7 shows the light-off and light-out temperatures for the Pd-Pt/Al<sub>2</sub>O<sub>3</sub> catalysts in fresh, deactivated, and reactivated state. As already described in previous sections, 15 h in a SO<sub>2</sub> containing stream led to pronounced deactivation shifting the light-off temperature with about 100 K to higher temperatures. Regeneration under lean conditions (heating up to 550 °C) only slightly recovered the activity, and it is more efficient in the presence of methane ("RM") than just O<sub>2</sub> and H<sub>2</sub>O in N<sub>2</sub> ("lean"). These results are in line with the work of Colussi et al. [21] who reported more effective SO<sub>2</sub> desorption under reaction conditions compared to inert conditions on a Pd/Al<sub>2</sub>O<sub>3</sub> catalyst. They explained the behavior by in situ production of H<sub>2</sub>O by the oxidation of CH<sub>4</sub> on Pd-sites leading to a better desorption of surface sulfates from alumina. Another explanation might be the higher temperature generated by the exothermic combustion of methane in case of the "RM" regeneration procedure. In the presence of CH<sub>4</sub>, the temperature at the outlet of the catalyst raised by 20 K compared to non-reactive conditions. This higher temperature very likely caused the slightly better regeneration performance under reactive conditions. However, as can be seen in Fig. 7, only small variations in T<sub>50</sub> were observed for lean regeneration conditions. The stability of poisoning sulfates is too high under oxygen containing conditions and thus cannot be decomposed at temperatures below 550 °C effectively [41,47]. Even at 650 °C only a small recovery was observed for similar catalyst compositions [23].

Much better regeneration results were observed under fuel rich conditions (Reg. (c) "rich" in Fig. 7). The poisoned Pd-Pt/Al<sub>2</sub>O<sub>3</sub> was regenerated completely and showed a T<sub>50</sub> slightly lower compared to the fresh state. The effectiveness of rich regeneration is well known from literature [20,25,27–29,48]. Arosio et al. [27] reported the desorption of SO<sub>2</sub> from a sulfated Pd/Al<sub>2</sub>O<sub>3</sub> under rich conditions (CH<sub>4</sub>, H<sub>2</sub>O in He) starting already at 400 °C. They also observed an increase in activity after rich treatment at 500 °C and higher temperatures. Furthermore, Luo et al. [47] showed on a Pt/Al<sub>2</sub>O<sub>3</sub> catalyst that the presence of H<sub>2</sub>O under reducing conditions leads to desorption of sulfur species at lower temperature compared to only H<sub>2</sub>. The promotional effect of water was discussed to be related to structural transformation of aluminum sulfates to (Al<sub>2</sub>O<sub>2</sub>)SO(OH) species lowering the desorption energy.

Although the activity is completely restored during the first heating after rich regeneration, constant deactivation occurred afterwards. This is reflected by the high T<sub>50</sub> during consecutive cooling, and caused by sulfur species spillover from Al<sub>2</sub>O<sub>3</sub>.

### 3.2.4. Catalytic performance and regeneration of Pd-Pt/CZ powder catalyst

Fig. 8 shows the activity of powdered Pd-Pt/CZ and monolithic Pd-Pt/Al<sub>2</sub>O<sub>3</sub> in fresh state and after 15 h in 5 ppm SO<sub>2</sub>, 30 ppm NO<sub>2</sub>, 120 ppm NO, 3200 ppm CH<sub>4</sub>, 10% O<sub>2</sub>, 12% H<sub>2</sub>O in N<sub>2</sub> at 450 °C. Already in the fresh state, the CZ supported sample demonstrates lower activity than Pd-Pt/Al<sub>2</sub>O<sub>3</sub>. The light-off temperature is 40 K

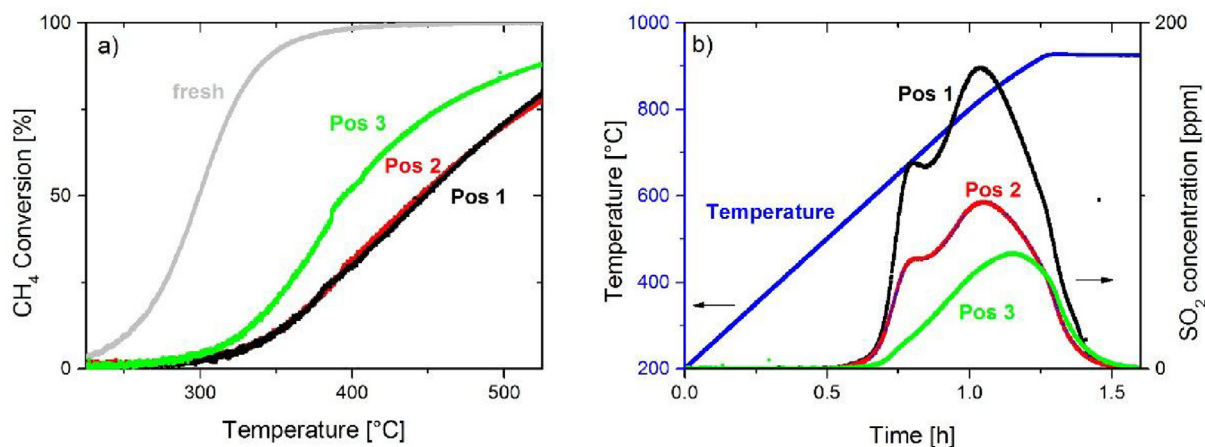
higher than for Pd-Pt/Al<sub>2</sub>O<sub>3</sub>. A higher noble metal loading of the Pd-Pt/Al<sub>2</sub>O<sub>3</sub> sample might be responsible. After 15 h in SO<sub>2</sub> containing atmosphere, the powdered Pd-Pt/CZ catalyst is highly deactivated. Only 17% methane was converted at 550 °C. Obviously, the CZ support was not able to maintain a high catalytic activity of the active Pd-Pt particles in SO<sub>2</sub> containing atmosphere, due to pronounced formation of sulfates on the active sites [34]. For pure ZrO<sub>2</sub>, only surface sulfates were observed while bulk sulfates were reported for CeO<sub>2</sub> and CeZrO<sub>x</sub> mixtures. Since our sample is a 60:30 (mass ratio) solid solution of ZrO<sub>2</sub> and CeO<sub>2</sub>, a sulfation behavior more influenced by ZrO<sub>2</sub> would be expected.

Since the reductive treatment was found to be very effective for regeneration of the SO<sub>2</sub> poisoned Pd-Pt/Al<sub>2</sub>O<sub>3</sub>, the same experiment was performed with powdered Pd-Pt/CZ. The results are shown in Fig. 9. For powdered Pd-Pt/CZ, an even increased activity after poisoning and consecutive rich regeneration compared to the fresh state is observed. This fact could be explained by a complete regeneration of sulfur-poisoned sites and accompanied reduction of the noble metals. The positive influence of reductive pretreatment on CH<sub>4</sub> oxidation activity of Pd based catalysts has also been reported in literature [49] and traced back to several effects, e.g. roughening of the particle surface [50], better interaction between Pd and Pt [17] and formation of metallic sites [51,52]. This enhanced activity is lost during the first light-off after rich regeneration as can be seen in Fig. 9, but the activity remained on the same level as for the fresh Pd-Pt/CZ during cooling. A S-TPD (Fig. S5) performed after rich regeneration and two following light-off experiments proved that sulfur species were still present on the Pd-Pt/CZ sample but decomposed only at temperatures above 700 °C. Thus, in contrast to the catalyst on Al<sub>2</sub>O<sub>3</sub> based support, the stable sulfur species on the CZ are not able to migrate to the active species at the tested temperatures.

Consequently, this catalyst was selected for more advanced tests to identify regeneration strategies under more engine relevant conditions. The experiments were performed with the powdered Pd-Pt/CZ catalyst in an atmosphere consisting of 5 ppm SO<sub>2</sub>, 30 ppm NO<sub>2</sub>, 120 ppm NO, 1000 ppm CH<sub>4</sub>, 10% O<sub>2</sub>, 12% H<sub>2</sub>O in N<sub>2</sub> at 450 °C over several hours until variations of only 1–2% of CH<sub>4</sub> conversion were observed. At that point, different short changes in gas atmosphere were induced. At first, the SO<sub>2</sub> dosage was stopped, which basically showed no effect on the activity. A temperature of 450 °C is certainly too low to recover the poisoned catalyst in sulfur free atmosphere, which is in agreement with the above reported experiments. Switching off the O<sub>2</sub> supply at 450 °C did not regenerate the catalyst either (Fig. S6). Because of this, changes in gas atmosphere were combined with increasing the temperature. As can be seen in Fig. 10, SO<sub>2</sub>-free lean reaction conditions are not able to regenerate the catalyst at temperatures up to 550 °C. During heating only a small increase in conversion is observed, which relates to the increased temperature. Nevertheless, the subsequent test at 450 °C showed no catalyst regeneration after this treatment.

Rich conditions realized by turning off the oxygen flow at 500 °C (48 h in Fig. 10) also did not influence the catalyst behavior. Only at 550 °C, rich treatment led to improved catalyst activity, although SO<sub>2</sub> was always present in the gas stream. Fig. 10b reveals the evolution of different gases during heating and during the rich atmosphere treatment at 550 °C. During heating, SO<sub>2</sub> desorbed from the catalyst surface, which was accompanied by a small increase in CH<sub>4</sub> conversion. At 550 °C, the oxygen shut-off led instantly to the decrease of NO and NO<sub>2</sub> concentration via CH<sub>4</sub> oxidation. After 1 h, 10% oxygen were added again to the gas stream at 550 °C. As soon as O<sub>2</sub> was present, the CH<sub>4</sub> conversion rose to almost 75% accompanied by an increase in NO concentration and a drop in SO<sub>2</sub> evolution. At 450 °C the conversion started at 26% and slowly decreased again over time.





**Fig. 13.** (a) Methane conversion as function of temperature of monolithic Pd-Pt/CZ in fresh state and after 60 h engine operation (3 engine operated samples corresponding to catalyst inlet, middle and outlet (Pos 1, 2, 3, Fig. 12)) during cooling. Gas composition for light-offs: 3200 ppm CH<sub>4</sub>, 10% O<sub>2</sub> in N<sub>2</sub>. Temperature ramp: 3 K/min. GHSV = 30,000 h<sup>-1</sup>. (b) Temperature-Programmed-Desorption of sulfur species (S-TPD) of monolithic Pd-Pt/CZ engine aged-samples. Gas composition: 5 L/min N<sub>2</sub>.

The evolution of SO<sub>2</sub> in Fig. 10b shows some interesting features. Even under lean conditions at temperatures above 450 °C SO<sub>2</sub> is desorbed from the surface, suggesting the decomposition of instable surface species or desorption of SO<sub>2</sub> adsorbed on different surface sites. However, the activity was still lower than in SO<sub>2</sub> free atmosphere at 550 °C. This indicates, that in SO<sub>2</sub> containing gas stream continuous poisoning of active sites takes place although SO<sub>2</sub> desorbs from the surface. During the rich phase, still a high amount of SO<sub>2</sub> was detected. This is in line with results from Luo et al. [47] who also observed SO<sub>2</sub> under reducing conditions. However, in presence of water also H<sub>2</sub>S and H<sub>2</sub>SO<sub>4</sub> is expected to be generated [28,47], which was not monitored in the present study. Such a behavior leads to the assumption that during one hour in rich conditions a high amount of sulfur species on the catalyst and especially on the active sites was decomposed leading to the high activity in consecutive lean phase. The sudden decay of SO<sub>2</sub> when changing to fuel lean conditions at 550 °C supports this assumption. In presence of O<sub>2</sub>, the SO<sub>2</sub> was oxidized to SO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> on freshly regenerated noble metal sites and stored again in form of sulfites or sulfates.

### 3.3. Catalyst at engine test bench

#### 3.3.1. Deactivation of monolithic Pd-Pt/CZ during engine operation

To investigate catalyst deactivation under real engine operation conditions, the corresponding washcoated Pd-Pt/CZ catalyst was tested for 60 h on a gas engine operating at  $\lambda = 1.68$ . As can be seen in Fig. 11, the methane conversion constantly decreased during operation resulting in only 20% after 60 h time on stream. Although the space velocity was higher during engine tests, the catalyst activity did not drop as fast as in the laboratory catalyst test. As discussed before, the concentration of sulfur in the gas stream has a crucial impact on the long-term activity decreasing faster with higher SO<sub>2</sub> concentration. Since the sulfur concentration in the engine exhaust-gas was below 0.3 ppm, a slower deactivation is expected.

The deactivated sample was divided into 3 different zones (inlet, middle, and outlet) and cylindrical cores were drilled out for further investigations in the laboratory. Fig. 12 depicts the positions and labelling of the samples.

The deactivation observed during engine operation was confirmed during experiments on catalyst test benches as depicted in Fig. 13a. For all positions along the catalyst, the CH<sub>4</sub> oxidation activity drastically decreased. Sample Pos 3 (catalyst outlet) exhibited

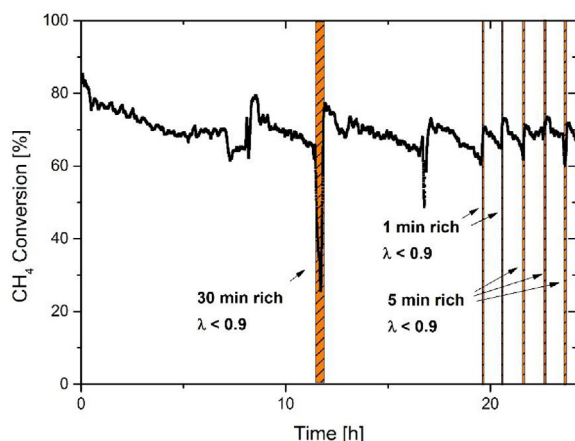
the highest activity among the deactivated samples. On contrary, there was no difference in activity between Pos 1 and Pos 2, which showed a poor activity due to the larger amount of stored sulfur species. From the TPD experiments (Fig. 13b) the desorption of the stored sulfur species on the catalyst can clearly be determined. The presence of sulfur species on the deactivated samples is not distributed homogeneously. Closer to the catalyst inlet, a higher sulfur amount was found. Lampert et al. [20] and Lanzerath et al. [30] did not report such a spatial dependency of sulfur amount along an engine tested catalyst. However, this might be due to the fact that the engine test in our study took place for only 60 h and with a low sulfur content, which was probably not sufficient for a complete saturation of the catalyst with sulfur species. Russell et al. [33] confirmed a spatial distribution of poisoning species depending on the total amount of SO<sub>2</sub> entering a Pt/Al<sub>2</sub>O<sub>3</sub> catalyst starting at the catalyst inlet.

Furthermore, Pos 1 and 2 exhibit an additional desorption peak at 680 °C, which is not present for Pos 3. Such a peak is not reported in literature. It may be linked to sulfur species that are responsible for the lower activity of Pos 1 and Pos 2 besides the generally higher sulfur concentration on Pos 1 and Pos 2.

#### 3.3.2. Regeneration of monolithic Pd-Pt/CZ during engine operation

Since it was found in the lab bench tests that regeneration of SO<sub>2</sub> poisoned catalysts is favored under rich conditions, an experiment was designed to investigate this issue under real engine conditions with a fresh monolithic Pd-Pt/CZ catalyst. The result of this test can be seen in Fig. 14. As already described above, the catalyst deactivated under lean conditions, due to poisoning by sulfur. After 12 h on stream, the engine controller was set at an increased fuel amount to cross the  $\lambda = 1$  limit. To keep the exhaust-gas temperature at 450 °C, the load was reduced, also lowering the space velocity towards 50,000 h<sup>-1</sup>. During this rich treatment for 30 min, the catalyst regenerated and a pronounced increase of the performance was obtained (Fig. 14). After ongoing deterioration of the catalyst, shorter rich pulses for 5 and 1 min were applied. These shorter rich phases also led to regeneration of the catalyst. Periodic switches to rich conditions for short times turned out to be an effective way to stabilize the conversion between 65 and 70%. At the same point of time on stream, the catalyst operating solely under lean conditions only exhibited 40% methane conversion.

Unlike in the transient regeneration experiment performed with powdered Pd-Pt/CZ on a catalyst lab test bench (Fig. 10), reductive treatment led to enhanced activity at the engine test bench already



**Fig. 14.** CH<sub>4</sub> conversion as function of time on a monolithic Pd-Pt/CZ catalyst operated on a gas engine running at  $\lambda = 1.68$  with switches to  $\lambda < 1$ . Gas composition under lean conditions can be found in Table 1. GHSV = 80,000 h<sup>-1</sup>. Temperature at catalyst inlet was kept constant at 450 °C. Areas marked as “rich” are realized by changing the operation point to fuel rich mixture generating reductive conditions in the exhaust. This also changed the GHSV to 50,000 h<sup>-1</sup>.

at 450 °C. This may be due to the following reasons. Firstly, the SO<sub>2</sub> concentration in the engine test is by factor 15 lower than in the catalyst regeneration experiment. Thus, the rate of desorption of sulfates during rich run can outbalance the re-poisoning which might not be possible at a higher SO<sub>2</sub> concentration. Secondly, the gas composition during rich treatment at the engine also contained other HCs, CO and most probably H<sub>2</sub> while in the laboratory catalyst test only CH<sub>4</sub> as reductive component was present. This variation in gas mixture can lead to a more efficient regeneration [29]. Thirdly, the reductive treatment might also have had a positive effect on unpoisoned noble metals by reduction/reoxidation as discussed in section 3.2.4. Even in sulfur-free conditions, reductive treatment was reported to have a positive effect on Pd based methane oxidation catalysts [49,51,52].

Strikingly, this experiment shows that regeneration during engine operation is possible. If the rich treatment is combined with an increase in exhaust-gas temperature, even better results are expected.

#### 4. Conclusions

SO<sub>2</sub> poisoning and catalyst regeneration strategies were investigated for the first time by combining lab-bench catalyst tests with gas engine experiments. The results obtained for the Pd-Pt/Al<sub>2</sub>O<sub>3</sub> and the Pd-Pt/CeO<sub>2</sub>-ZrO<sub>2</sub>-Y<sub>2</sub>O<sub>3</sub>-La<sub>2</sub>O<sub>3</sub> catalyst pointed out the following main aspects:

- (1) The rate of deactivation depends on SO<sub>2</sub> concentration in the gas stream. Even small amounts of sulfur species (<0.3 ppm) lead to accumulation of sulfur on methane oxidation catalysts and cause rapid deactivation under standard lean burn gas engine conditions.
- (2) The amount and stability of the SO<sub>2</sub>-derived species are strongly influenced by the poisoning temperature. Thus, poisoning at 400 °C leads to more distinct deactivation of Pd-Pt/Al<sub>2</sub>O<sub>3</sub>. However, poisoning at 450 °C leads to more durable poisoning caused by formation of stronger bound sulfates.
- (3) A higher pressure, characteristic for pre-turbo positioning, leads to higher uptake of sulfur species while the activity is higher due to longer residence time at 450 °C. At 600 °C, the activity remains high over 20 h. However, at this temperature

some poisoning still takes place, which results in lower activity in consecutive light-offs.

- (4) Fuel rich conditions, even for short time, combined with temperatures above 500 °C were found to be most efficient for catalyst regeneration due to decomposition of surface sulfates and desorption of SO<sub>2</sub>.
- (5) A successful first attempt was made to transfer the results from laboratory catalyst test and to regenerate a methane oxidation catalyst during engine operation. This was achieved by changing from a lean operation point of the gas engine to a fuel rich point at 450 °C. The mounted catalyst instantly provided higher activity after the rich treatment. Short rich pulses every 30 min stabilized the CH<sub>4</sub> conversion at about 65–70%.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2017.06.048>.

#### References

- [1] O. Deutschmann, J.-D. Grunwaldt, Exhaust Gas Aftertreatment in Mobile Systems: Status, Challenges, and Perspectives, *Chem. Ing. Tech.* 85 (2013) 595–617.
- [2] R.J. Farrauto, J.K. Lampert, M.C. Hobson, E.M. Waterman, Thermal decomposition and reformation of PdO catalysts; support effects, *Appl. Catal. B* 6 (1995) 263–270.
- [3] P. Gélín, M. Primet, Complete oxidation of methane at low temperature over noble metal based catalysts: a review, *Appl. Catal. B* 39 (2002) 1–37.
- [4] A. Gärtner, T. Lenk, R. Kiemel, S. Casu, C. Breuer, K. Stöwe, High-throughput Screening Approach to Identify New Catalysts for Total Oxidation of Methane from Gas Fueled Lean Burn Engines, *Top. Catal.* 59 (2016) 1071–1075.
- [5] D. Ciuparu, M.R. Lyubovsky, E. Altman, L.D. Pfefferle, A. Datye, Catalytic combustion of methane over palladium-based catalysts, *Catal. Rev. – Sci. Eng.* 44 (2002) 593–649.
- [6] P. Gélín, L. Urfels, M. Primet, E. Tena, Complete oxidation of methane at low temperature over Pt and Pd catalysts for the abatement of lean-burn natural gas fuelled vehicles emissions: influence of water and sulphur containing compounds, *Catal. Today* 83 (2003) 45–57.
- [7] K.-i. Fujimoto, F.H. Ribeiro, M. Avalos-Borja, E. Iglesia, Structure and Reactivity of PdO<sub>x</sub>/ZrO<sub>2</sub> Catalysts for Methane Oxidation at Low Temperatures, *J. Catal.* 179 (1998) 431–442.
- [8] A.K. Datye, J. Bravo, T.R. Nelson, P. Atanasova, M. Lyubovsky, L. Pfefferle, Catalyst microstructure and methane oxidation reactivity during the Pd ↔ PdO transformation on alumina supports, *Appl. Catal. A* 198 (2000) 179–196.
- [9] S. Colussi, A. Trovarelli, G. Groppi, J. Llorca, The effect of CeO<sub>2</sub> on the dynamics of Pd-PdO transformation over Pd/Al<sub>2</sub>O<sub>3</sub> combustion catalysts, *Catal. Commun.* 8 (2007) 1263–1266.
- [10] J.-D. Grunwaldt, N. van Vegten, A. Baiker, Insight into the structure of supported palladium catalysts during the total oxidation of methane, *Chem. Commun.* (2007) 4635–4637.
- [11] N.M. Kinnunen, J.T. Hirvi, M. Suvanto, T.A. Pakkanen, Role of the Interface between Pd and PdO in Methane Dissociation, *J. Phys. Chem. C* 115 (2011) 19197–19202.
- [12] G. Lapisardi, L. Urfels, P. Gelin, M. Primet, A. Kaddouri, E. Garbowski, S. Toppi, E. Tena, Superior catalytic behaviour of Pt-doped Pd catalysts in the complete oxidation of methane at low temperature, *Catal. Today* 117 (2006) 564–568.

- [13] K. Narui, H. Yata, K. Furuta, A. Nishida, Y. Kohtoku, T. Matsuzaki, Effects of addition of Pt to PdO/Al<sub>2</sub>O<sub>3</sub> catalyst on catalytic activity for methane combustion and TEM observations of supported particles, *Appl. Catal. A* 179 (1999) 165–173.
- [14] R. Strobel, S.E. Pratsinis, A. Baiker, Flame-made Pd/La<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> nanoparticles: thermal stability and catalytic behavior in methane combustion, *J. Mater. Chem.* 15 (2005) 605–610.
- [15] R. Burch, F.J. Urbano, P.K. Loader, Methane combustion over palladium catalysts: the effect of carbon dioxide and water on activity, *Appl. Catal. A* 123 (1995) 173–184.
- [16] P. Hurtado, S. Ordóñez, H. Sastre, F. Diez, Combustion of methane over palladium catalyst in the presence of inorganic compounds: inhibition and deactivation phenomena, *Appl. Catal. B* 47 (2004) 85–93.
- [17] A.T. Gremminger, H.W. Pereira de Carvalho, R. Popescu, J.-D. Grunwaldt, O. Deutschmann, Influence of gas composition on activity and durability of bimetallic Pd–Pt/Al<sub>2</sub>O<sub>3</sub> catalysts for total oxidation of methane, *Catal. Today* 258 (2015) 470–480.
- [18] W.R. Schwartz, D. Ciuparu, L.D. Pfefferle, Combustion of Methane over Palladium-Based Catalysts: Catalytic Deactivation and Role of the Support, *J. Phys. Chem. C* 116 (2012) 8587–8593.
- [19] B. Torkashvand, A. Gremminger, S. Valchera, M. Casapu, J.-D. Grunwaldt, O. Deutschmann, The Impact of Pre-turbine Catalyst Placement on Methane Oxidation in Lean-burn Gas Engines: An Experimental and Numerical Study, *SAE Technical Paper* 2017-03-28, 2017.
- [20] J.K. Lampert, M.S. Kazi, R.J. Farrauto, Methane Emissions Abatement from Lean Burn Natural Gas Vehicle Exhaust: Sulfur's Impact on Catalyst Performance, *SAE Technical Paper* 961971, 1996.
- [21] S. Colussi, F. Arosio, T. Montanari, G. Busca, G. Groppi, A. Trovarelli, Study of sulfur poisoning on Pd/Al<sub>2</sub>O<sub>3</sub> and Pd/CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> methane combustion catalysts, *Catal. Today* 155 (2010) 59–65.
- [22] L.J. Hoyos, H. Praliud, M. Primet, Catalytic combustion of methane over palladium supported on alumina and silica in presence of hydrogen sulfide, *Appl. Catal. A* 98 (1993) 125–138.
- [23] J.K. Lampert, M.S. Kazi, R.J. Farrauto, Palladium catalyst performance for methane emissions abatement from lean burn natural gas vehicles, *Appl. Catal. B* 14 (1997) 211–223.
- [24] M.S. Wilburn, W.S. Epling, SO<sub>2</sub> adsorption and desorption characteristics of Pd and Pt catalysts: Precious metal crystallite size dependence, *Appl. Catal. A* 534 (2017) 85–93.
- [25] J.M. Jones, V.A. Dupont, R. Brydson, D.J. Fullerton, N.S. Nasri, A.B. Ross, A.V.K. Westwood, Sulphur poisoning and regeneration of precious metal catalysed methane combustion, *Catal. Today* 81 (2003) 589–601.
- [26] S. Ordóñez, P. Hurtado, F. Diez, Methane catalytic combustion over Pd/Al<sub>2</sub>O<sub>3</sub> in presence of sulphur dioxide: development of a regeneration procedure, *Catal. Lett.* 100 (2005) 27–34.
- [27] F. Arosio, S. Colussi, G. Groppi, A. Trovarelli, Regeneration of S-poisoned Pd/Al<sub>2</sub>O<sub>3</sub> catalysts for the combustion of methane, *Catal. Today* 117 (2006) 569–576.
- [28] N. Ottinger, R. Veele, Y. Xi, Z.G. Liu, Desulfation of Pd-based Oxidation Catalysts for Lean-burn Natural Gas and Dual-fuel Applications, *SAE Technical Paper* 2015-01-0991, 2015.
- [29] Y. Xi, N. Ottinger, Z.G. Liu, Effect of Reductive Regeneration Conditions on Reactivity and Stability of a Pd-Based Oxidation Catalyst for Lean-Burn Natural Gas Applications, *SAE Technical Paper* 2016- 04-05, 2016.
- [30] P. Lanzerath, A. Traebert, A. Massner, U. Gaertner, Investigations on Chemical Ageing of Diesel Oxidation Catalysts and Coated Diesel Particulate Filters, *SAE Technical Paper* 2010-04-12, 2010.
- [31] S. Brunauer, P.H. Emmett, E. Teller, Adsorption of gases in multimolecular layers, *J. Am. Chem. Soc.* 60 (1938) 309–319.
- [32] J. Günter, J. Pesek, K. Schäfer, A. Bertótné Abai, M. Casapu, O. Deutschmann, J.-D. Grunwaldt, Cu-SSZ-13 as pre-turbine NO<sub>x</sub>-removal-catalyst: Impact of pressure and catalyst poisons, *Appl. Catal. B* 198 (2016) 548–557.
- [33] A. Russell, C. Henry, N.W. Currier, A. Yezerets, W.S. Epling, Spatially resolved temperature and gas species concentration changes during C<sub>3</sub>H<sub>6</sub> oxidation over a Pt/Al<sub>2</sub>O<sub>3</sub> catalyst following sulfur exposure, *Appl. Catal. A* 397 (2011) 272–284.
- [34] T. Luo, R.J. Gorte, Characterization of SO<sub>2</sub>-poisoned ceria-zirconia mixed oxides, *Appl. Catal. B* 53 (2004) 77–85.
- [35] J. Chen, H. Arandiyani, X. Gao, J. Li, Recent Advances in Catalysts for Methane Combustion, *Catal. Surv. Asia* 19 (2015) 140–171.
- [36] S. Ordóñez, P. Hurtado, H. Sastre, F.V. Diez, Methane catalytic combustion over Pd/Al<sub>2</sub>O<sub>3</sub> in presence of sulphur dioxide: development of a deactivation model, *Appl. Catal. A* 259 (2004) 41–48.
- [37] J.H. Lee, D.L. Trimm, N.W. Cant, The catalytic combustion of methane and hydrogen sulphide, *Catal. Today* 47 (1999) 353–357.
- [38] D.L. Mowery, R.L. McCormick, Deactivation of alumina supported and unsupported PdO methane oxidation catalyst: the effect of water on sulfate poisoning, *Appl. Catal. B* 34 (2001) 287–297.
- [39] T.C. Yu, H. Shaw, The effect of sulfur poisoning on methane oxidation over palladium supported on gamma-alumina catalysts, *Appl. Catal. B* 18 (1998) 105–114.
- [40] O. Kröcher, M. Widmer, M. Elsener, D. Rothe, Adsorption and Desorption of SO<sub>x</sub> on Diesel Oxidation Catalysts, *Ind. Eng. Chem. Res.* 48 (2009) 9847–9857.
- [41] T. Hamzehlouyan, C.S. Sampara, J. Li, A. Kumar, W.S. Epling, Kinetic study of adsorption and desorption of SO<sub>2</sub> over γ-Al<sub>2</sub>O<sub>3</sub> and Pt/γ-Al<sub>2</sub>O<sub>3</sub>, *Appl. Catal. B* 181 (2016) 587–598.
- [42] R. Gholami, M. Alyani, K. Smith, Deactivation of Pd Catalysts by Water during Low Temperature Methane Oxidation Relevant to Natural Gas Vehicle Converters, *Catalysts* 5 (2015) 561–594.
- [43] M.N. Subramaniam, C. Hayes, D. Tomazic, M. Downey, C. Bruestle, Pre-Turbo Aftertreatment Position for Large Bore Diesel Engines - Compact & Cost-Effective Aftertreatment with a Fuel Consumption Advantage, *SAE Int. J. Engines* 4 (2011) 106–116.
- [44] C.N. Satterfield, *Heterogeneous catalysis in practice*, McGraw-Hill, New-York, 1980.
- [45] X. Auvray, T. Pingel, E. Olsson, L. Olsson, The effect gas composition during thermal aging on the dispersion and NO oxidation activity over Pt/Al<sub>2</sub>O<sub>3</sub> catalysts, *Appl. Catal. B* 129 (2013) 517–527.
- [46] M. Monai, T. Montini, M. Melchionna, T. Duchoñ, P. Kúš, C. Chen, N. Tsud, L. Nasi, K.C. Prince, K. Veltruská, V. Matolín, M.M. Khader, R.J. Gorte, P. Fornasiero, The effect of sulfur dioxide on the activity of hierarchical Pd-based catalysts in methane combustion, *Appl. Catal. B* 202 (2017) 72–83.
- [47] J.-Y. Luo, D. Kisinger, A. Abedi, W.S. Epling, Sulfur release from a model Pt/Al<sub>2</sub>O<sub>3</sub> diesel oxidation catalyst: Temperature-programmed and step-response techniques characterization, *Appl. Catal. A* 383 (2010) 182–191.
- [48] F. Arosio, S. Colussi, A. Trovarelli, G. Groppi, Effect of alternate CH<sub>4</sub>-reducing/lean combustion treatments on the reactivity of fresh and S-poisoned Pd/CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts, *Appl. Catal. B* 80 (2008) 335–342.
- [49] C.F. Cullis, B.M. Willatt, Oxidation of methane over supported precious metal catalysts, *J. Catal.* 83 (1983) 267–285.
- [50] R.S. Monteiro, D. Zemlyanov, J.M. Storey, F.H. Ribeiro, Turnover Rate and Reaction Orders for the Complete Oxidation of Methane on a Palladium Foil in Excess Dioxygen, *J. Catal.* 199 (2001) 291–301.
- [51] A. Ersson, H. Kusar, R. Carroni, T. Griffin, S. Jaras, Catalytic combustion of methane over bimetallic catalysts a comparison between a novel annular reactor and a high-pressure reactor, *Catal. Today* 83 (2003) 265–277.
- [52] A. Hellman, A. Resta, N.M. Martin, J. Gustafson, A. Trincherro, P.A. Carlsson, O. Balmes, R. Felici, R. van Rijn, J.W.M. Frenken, J.N. Andersen, E. Lundgren, H. Grönbeck, The Active Phase of Palladium during Methane Oxidation, *J. Phys. Chem. Lett.* 3 (2012) 678–682.